

**REACTIONS OF GAS-PHASE IONS
STUDIED BY
THE CHARGE TRANSFER TECHNIQUE**

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This review gives a summary and discussion of the results from the following papers which will be referred to by the Roman numerals I-VI.

- I. J. Sunner and I. Szabo
Charge transfer mass spectra of isomers.
I. $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$.
Int. J. Mass Spectrom. Ion Phys., Vol. 25, No. 3, in press.
- II. J. Sunner and I. Szabo
Charge transfer mass spectra of isomers.
II. $n\text{-C}_3\text{H}_7\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$.
Int. J. Mass Spectrom. Ion Phys., Vol. 25, No. 3, in press.
- III. J. Sunner
Charge transfer mass spectra of isomers.
III. Cis- and trans-2-butene.
Submitted to the Int. J. Mass Spectrom. Ion Phys.
- IV. J. Sunner and I. Szabo
Charge transfer mass spectra of N_2O .
Ion-molecule reactions in N_2O .
To be submitted to the Int. J. Mass Spectrom. Ion. Phys.
- V. J. Sunner and I. Szabo
Ion-molecule reactions in H_2O after charge transfer ionization.
To be submitted to the Int. J. Mass Spectrom. Ion. Phys.
- VI. J. Sunner and I. Szabo
The analytical use of chemical ionization in a tandem mass spectrometer.
Advances in Mass Spectrometry, Vol. 7, N. Daly (Ed.), Heyden, London, 1977, in press.



1. INTRODUCTION

In mass spectrometric investigations of uni- and bimolecular reactions of gas-phase ions, it is of prime importance to know the internal energy of the ionic reactant. In ionization by electron and photon impact, molecular ions are formed with a wide distribution of internal energies, which is usually not accurately known. However, when using the *charge transfer technique* [1,2], which utilizes ion-impact ionization, monoenergetic excitation of ions is achieved. This method, for preparing ions in specified electronic states or with a specified excitation energy, was developed by Lindholm [3]. It has since 1954 contributed to the understanding of ionic fragmentations and reactions of molecule ions in excited states. Breakdown graphs, i.e. the mass spectrum of a compound as a function of ionization energy, had earlier been determined by Lindholm's group for about 25 molecules [1]. Consecutive ion-molecule reactions (IMRs) of primary fragment ions have also been investigated in a number of simple gases [1].

The results presented in this thesis have been obtained with the charge transfer method of ionization. They may be divided into three main topics:

1. Unimolecular reactions of excited molecular ions, i.e. breakdown graphs (Papers I-IV).
2. Ion-molecule reactions (Papers I, IV and V).
3. Analytical application of chemical ionization in a tandem mass spectrometer (Paper VI).

Four new breakdown graphs were determined in this thesis. Papers I and II concern i-butane and i-propanol. Earlier, n-butane [4] and n-propanol [5] had been investigated with the same technique. Together these breakdown graphs are the first ones for structural isomers determined over a large energy range. In paper III the breakdown graph for cis-2-butene is given. No differences were found relative to the graph for the trans isomer. Nonetheless,

different charge transfer mass spectra of these stereoisomers were obtained with some of the incident ions. The breakdown graph of N_2O is given in paper IV and the fragmentation of H_2O^+ is discussed in paper V.

The results of investigations on ion-molecule reactions in the i-butane, nitrous oxide and water systems are presented in papers I, IV and V, respectively.

The analytical application of the charge transfer technique is new and was first presented in paper VI. This technique will be referred to here as "Beam Chemical Ionization", *BCI*. It is one of the "soft" ionization methods, which for some years have been a focus of interest [6]. In contrast to chemical ionization in a high pressure ion source [7], the choice of a reagent ion in beam chemical ionization is almost unlimited.

In this summary, the charge transfer technique is shortly presented in the next section, 2. Because the results in papers I-III are discussed in the context of the quasi-equilibrium theory of mass spectra, an outline of this theory is given in Section 3. The results in this thesis concerning breakdown graphs, ion-molecule reactions and the method of beam chemical ionization are then summarized and discussed in Sections 4,5 and 6, respectively.

2. THE CHARGE TRANSFER TECHNIQUE

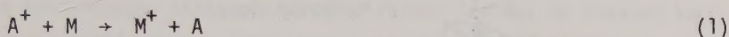
The charge transfer method has been reviewed by Lindholm [1], and only a brief outline of the apparatus, the energetics and the interpretation of mass spectra will be given here.

The experiments are performed in a tandem mass spectrometer of perpendicular type (Fig. 1). The incident ions are produced in the first mass spectrometer and pass the reaction chamber with a kinetic energy that can be varied from 900 to ca. 2 eV.

The ionized fragments produced as a result of the reactions between the incident ions and gas molecules are analysed in a second mass spectrometer, in a direction perpendicular to the incident ion beam.

Molecules in the reaction chamber may be ionized, not only by transfer of an electron, but also by transfer of a proton or a hydride-ion or by other ion-molecule reactions.

For the ionization of a molecule M, by a charge transfer reaction with an incident ion A^+



energy conservation requires that

$$E_{\text{exc}} = RE(A^+) - IP(M) - \Delta E \quad (2)$$

$RE(A^+)$ is the recombination energy of A^+ , that is the energy released by A^+ in the recombination with an electron; $IP(M)$ is the adiabatic ionization potential of M; E_{exc} is the excitation energy of M^+ and ΔE denotes the change in the total kinetic energy in the reaction.

Charge transfer reactions (eqn. 1), which take place with little or no momentum transfer, leave the M^+ ions with close to thermal kinetic energies and the ΔE values are practically zero. These ions formed with small initial kinetic energies, are preferably studied in a tandem mass spectrometer of perpendicular type (Fig. 1). This instrument discriminates against reactions involving momentum transfer. Thus mainly ions that result from charge transfer reactions that are close to resonant, should be observed. This assumption is basic to the charge transfer technique. That it is generally correct, is strongly supported by the overall success of the technique, especially for determining breakdown graphs. The validity of the assumption will, for a specific charge transfer reaction, be determined

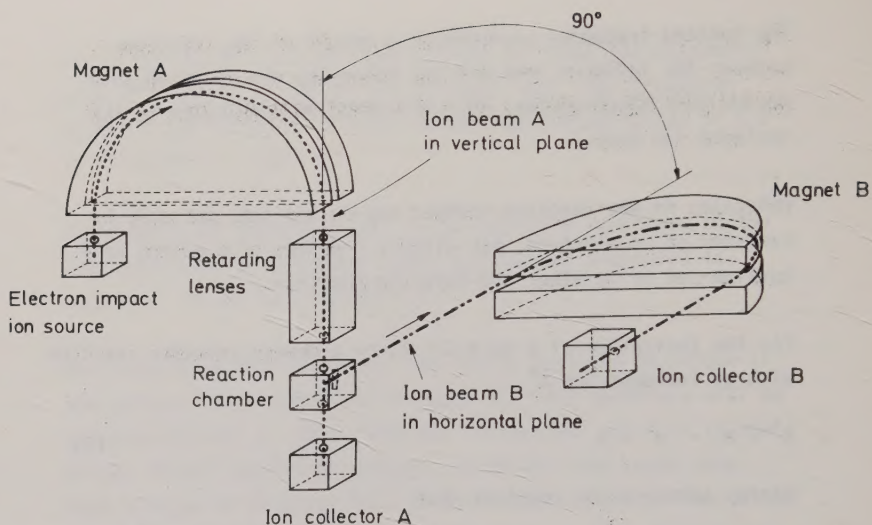


Fig. 1. Tandem mass spectrometer of perpendicular type used in Lund. The instrument was moved from Lindholm's laboratory in Stockholm in 1972 and has earlier been described by him [1].

by the dynamics of the reaction and the properties of the tandem mass spectrometer. Examples of cases where the assumption apparently fails are given in paper V. The topic is also discussed in connection with the $\text{Ar}^+ + \text{N}_2\text{O}$ experiments in paper IV. That exothermic charge transfer reactions are sometimes observed in a perpendicular type tandem mass spectrometer has been shown by kinetic analysis of the products [8].

A tandem mass spectrometer of perpendicular type particularly discriminates against endothermic reactions. The reason is that energy and momentum conservation requires that the primary products are scattered in the direction of the incident ions.

In Lindholm's laboratory, a large number of incident ions were used. A compilation of REs is given in ref. [1].

The observed mass spectra are as a rule mainly due to charge transfer reactions that are close to resonant. However other processes, for example proton and hydride-ion transfer, may contribute. Fortunately, the contributions from these processes are usually small, but often the mass spectra are corrected before they are used for the construction of the breakdown graph. This topic is discussed in more detail in papers I and III.

3. THE QUASI-EQUILIBRIUM THEORY

In mass spectrometry, unimolecular reactions are studied at such a low pressure that an initially formed ion may be treated as an isolated system. Ionization methods produce molecular ions often with such high excitation energies, that they decompose not only by several competing reaction pathways, but also in consecutive reactions in each pathway. An observed mass spectrum is the result of such a reaction scheme after a certain reaction time, usually in the order of microseconds. Most fragmentations are completed within this time. Metastable peaks in the mass spectrum are due to ions that dissociate between the reaction chamber and the magnetic analyser.

The molecules studied in papers I-III are large in the sense that the fragmentation of the molecular ions may be described by the quasi-equilibrium theory (QET) of mass spectra. The breakdown graphs are discussed in the context of this theory in the next section. For this reason a short account of the QET is given here. For a detailed treatment the reader is referred to Forst [9].

The QET was originally proposed in 1952 by Rosenstock, Wallenstein, Wahrhaftig and Eyring [10]. It is equivalent to the RRKM (Rice-Ramsperger-Kassel-Marcus) theory [9]. The QET is a statistical rate theory with a transition state formalism, which avoids descriptions of molecular dynamics. The following assumptions are made in the QET [9,11,12]:

1. The time of interaction leading to the formation of an ion is short compared to the time required for the subsequent fragmentations. The processes may thus be treated separately[†].
2. The rate of dissociation of the ion is slow relative to the rate of re-distribution of energy among the internal degrees of freedom, both electronic and vibrational, of the ion.
3. Each dissociation process may be described as a motion along a reaction coordinate separable from all other internal coordinates through a critical "activated complex" configuration.

The rate constant for the dissociation of a rotationless ion with the excitation energy E , over an activated complex with a minimum energy of E_0 is given by [9]:

$$k(E) = \frac{\alpha}{h} \times \frac{G^*(E-E_0)}{N(E)} \quad (3)$$

α is the reaction path degeneracy; h is Planck's constant; $N(E)$ is the density of vibrational states for the reactant and $G^*(E-E_0)$ is the integrated density for the transition state. Counting of states and assignment of molecular parameters for the transition states is thus essential to the calculation.

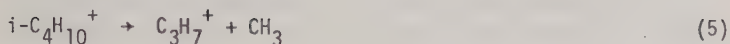
The decomposition,



requires a rearrangement of the parent ion. The activated complex is "tight", i.e. it has high vibrational frequencies and a low density of states [13]. The rate constant for reaction (4) is thus low (cf. eqn. 3). In contrast to this, the

[†]This is not obvious for charge transfer ionization. The collision time with incident ions of a few eV kinetic energy is ca. 10^{-13} s, i.e. the same order of magnitude as a vibrational period.

fragmentation,



occurs via breaking of a single bond. The corresponding activated complex is "loose", i.e. it has low vibrational frequencies and a high density of states [13]. The critical energy, E_0 , is somewhat higher than for reaction (4). The differences between the activated complexes thus explain why C_3H_6^+ is observed, only within a narrow energy range, and at low ionization energies in the breakdown graph of i-butane (Paper I).

4. RESULTS ON UNIMOLECULAR REACTIONS

4.1 The breakdown graphs of i-butane, i-propanol and cis-2-butene

The purpose of these studies was to compare the fragmentations of molecular ions of isomeric compounds. For the butanes and the propanols breakdown graphs, calculated with the QET, were available. The agreement between theory and experiment was satisfactory at excitation energies up to 5-6 eV, but disagreement was obvious at higher energies. In particular for the propanols it is apparent from the curves that several new fragmentation pathways must be included in the calculations. Some examples were mentioned in paper II. The breakdown graphs in papers I-III can hardly be used to test the validity of the QET, but rather to improve the application of the theory to real systems. Our result implies that the QET calculations can be improved in order to obtain better agreement with the experimental breakdown graphs. This will contribute to the understanding of the fragmentations of alkanes, alcohols and alkenes.

It was suggested by Vestal in his review of QET [13], that isomerization between the butane and the propanol molecular ions, respectively, is important in the fragmentation. Isomerization should preferably be observed at low excitation energies because the associated activated complex is most probably a "tight" one. However, as pointed out in paper I, comparison between the

breakdown graphs for the butanes suggest that isomerization if it occurs is of minor importance. The same conclusion applies for the propanols in paper II.

The assumption of rapid internal conversion of electronic to vibrational internal energy is not essential to the QET. Few examples of incomplete conversion have been proven, and benzene molecule ions may be the only example [14]. A prerequisite for the rapid internal conversion is that the potential energy surfaces are close to each other in energy (p.295 in ref. [9]). As seen from the photoelectron spectra this condition is fulfilled for the butanes and the propanols. However, in the photoelectron spectrum of cis-2-butene, there is a gap between 11 and 12 eV. It can thus not be taken for granted, that internal conversion to the electronic ground state is rapid enough, for all fragmentations to occur from this state.

In the breakdown graph of cis-2-butene (Paper III) five first generation fragment ions, $C_3H_5^+$, $C_4H_7^+$, $C_2H_4^+$, $C_4H_6^+$ and $C_3H_4^+$, have approximately the same appearance potentials. The three first fragments may be formed by breaking a single bond, but formation of the two latter requires rearrangements. The relative intensities do not change considerably between 12 and 15 eV. This is surprising, as according to the QET, rate constants for competing reactions are expected to have different energy dependencies. In particular, the transition states for formation of $C_4H_6^+$ and $C_3H_4^+$ should be "tight". Therefore their relative abundancies should decrease with increasing ionization energy.

Little is known about the competition between fragmentation of, and isomerization between molecule ions of different C_4H_8 isomers. That the breakdown graph of cyclobutane is different from that of 2-butene has been confirmed by Lifshitz and Tiernan [15]. The subject is of interest and deserves further study.

That different charge transfer mass spectra of cis and trans-2-butene were obtained for some incident ions is of interest for the analytical applications and this is discussed in Section 6.

A common feature of all breakdown graphs in papers I-III, is the constancy of the fragmentation patterns above ca. 17 eV. Independent determinations with photoionization techniques would be valuable in order to decide whether resonant charge transfer reactions are observed also at these high ionization energies. As long as this is not clear, it is maybe premature to pursue a discussion of the high-energy behaviour of the breakdown graphs too far. It seems however that the validity of the QET for highly excited species ($E_{\text{exc}} > 10$ eV) is not well known. Apart from the possibility of deviations from the QET, it is also possible that the ionization occurs directly to a repulsive potential energy surface. Alternatively, the fragmentation process is so fast that it can not be treated separately from the charge transfer reaction.

Fragment 41, C_3H_5^+ , shows a noteworthy behaviour at high energy in the breakdown graphs in papers I-III. In the case of the butanes and propane [16] (and apparently the propanols) the intensity does not decrease smoothly to zero but show a steplike behaviour above ca. 16 eV ionization energy. This was discussed in paper I. In contrast to this, the curve for the fragment in the breakdown graph of cis-2-butene decrease to zero at ca. 16 eV ionization energy. In this case, C_3H_5^+ is a second generation fragment directly formed from C_4H_8^+ , whereas in the case of the butanes it is a third generation fragment formed from $\text{C}_4\text{H}_{10}^+$ via C_3H_7^+ . In addition to the possible explanations given in paper I for the steplike behaviour of the fragment curve, it is possible that C_3H_5^+ is formed by alternative reactions, for example by successive expulsions of $\text{CH}_3 + 2\text{H}$ or $\text{CH}_2 + \text{H}_2 + \text{H}$ instead of $\text{CH}_3 + \text{H}_2$. This explanation is not likely, as the calculated appearance potentials for the two former processes are 17.2 and 17.5 eV, respectively [17]. Alternatively, C_3H_5^+ is formed in a structure with a high stability or the excess energy is removed as kinetic energy of the products.

4.2 Fragmentation of N_2O

The ionization and fragmentation of "small" positive molecule ions are generally rather complex (cf. paper IV and refs. therein). The understanding of these processes depends on a detailed knowledge of potential energy surfaces and their intersections.

With photon and electron impact on a molecule direct vertical Franck-Condon transitions occur to attractive and repulsive potential energy surfaces of the neutral molecule and the positive ion. Ion states may also be populated by autoionization of neutral states, for example Rydberg states converging to vibrationally excited ion states. Fragmentation results from transitions to repulsive ion states or attractive states above a dissociation limit. Predissociation occurs from bound (e.g. metastable) states by curve crossing. The possibility of ion-pair production further complicates the interpretation of the obtained mass spectra.

With charge transfer ionization, autoionization and ion-pair production is not possible. Because of this, the number of alternative fragmentation pathways for the production of an observed fragment is considerably reduced. Despite that the collision time at a few eV kinetic energy of the incident ions, is of the same order of magnitude as a vibrational period, Franck-Condon factors are still important (see for example ref. [18]). Due to the polarization of the molecule in the presence of the ion, the Franck-Condon envelope may, however, become distorted [19]. Vibrational states that are not populated in direct transitions with electron and photon impact, may thus be accessible in charge transfer reactions.

Results on the fragmentation of N_2O^+

The fragmentation of N_2O^+ was investigated in Paper IV. Earlier the ionization and fragmentation processes of N_2O have been extensively investigated. Quantum mechanical calculations have also made a considerable contribution to the understanding of these processes [20].

The result of the charge transfer investigation was presented in the form of a breakdown graph in Paper IV. Some energy regions were not accessible with charge transfer. Consequently, the fragment ion curves were not drawn with continuous lines, but interruptions were made at gaps in the photoelectron spectrum. An exception was made for energies above the $\tilde{C}$ state at 20.1 eV, where little is known about which electronic states may be populated. In addition to the discussion in Paper IV, only a few comments will be made here.

Different mechanisms have been proposed for the formation of NO^+ between 15.01 and 16.39 eV [21,22]. According to Brundle and Turner [21], Rydberg states predissociate to a neutral state, ($\tilde{C}'$), which subsequently autoionizes. Alternatively, vibrationally excited $\tilde{X}$ states of the ion may be involved [22,23]. If the metastable peak for the reaction, $N_2O^+ \rightarrow NO^+ + N$, observed above 15.1 eV [23] is in reality due to a monomolecular process [23,24] highly excited $\tilde{X}$ states must be involved. These may be formed via internal conversion and autoionization from Rydberg states and/or other neutral states [22,23]. Analogous processes from Rydberg states between 13.9 and 15 eV are indicated by the second order pressure dependence of the photoionization efficiency curve of NO^+ from N_2O , at energies corresponding to these states, but not to low vibrational states of N_2O^+ in the $\tilde{X}$ state [22]. The fragmentation pattern for vibrational levels of N_2O^+ in the $\tilde{X}$ state is therefore of considerable interest. The attempt to attain these levels, which are far outside the Franck-Condon region, by charge transfer with incident Ar^+ ions failed. This contradicts the assumption made in several papers [23,25,26] that this charge transfer reaction is actually resonant. The conclusions based on this assumption [25,26] are therefore questionable.

The result for N_2O^+ in the $\tilde{A}$ state agrees with the photoelectron-photoion coincidence study by Eland [27] for this energy region, as far as N_2O^+ and NO^+ is concerned. The O^+ fragment was not reported in the paper by Eland; and it could not be observed in

the photoionization efficiency curve [28] due to superimposed autoionization structure. Fragmentation occurs via predissociation to the same $\tilde{B}_2^-$ surface that is responsible for the NO^+ formation, and that was theoretically studied by Pipano and Kaufman [29]. The branching ratio between the dissociations to NO^+ and O^+ is ca. 4:1.

The fragmentation pattern for the $\tilde{B}$ state and states with higher energy constitutes new information. No N^+ is formed from the lower vibrational levels of the $\tilde{C}$ state. This shows that the repulsive $^2\Pi$ surface with the dissociation limit, $\text{N}^+ + \text{NO}$ in their ground states, at 19.47 eV [30], is not reached from the lower vibrational states. This is analogous to the situation for the $\tilde{A}$ state, relative to fragmentation to NO^+ [27]. There is a large number of excited states at high excitation energy. However, a straightforward explanation for the formation of N^+ above ca. 20 eV is that it occurs, either via a direct transition to the repulsive $^2\Pi$ surface mentioned above, or via a predissociation from a vibrationally excited $\text{N}_2\text{O}^+ \tilde{C}$ state.

5. ION-MOLECULE REACTIONS - DISCUSSION OF RESULTS

The charge transfer technique is suitable for investigating reactions of ions in excited electronic states. Apart from the improved definition of the energetic state of the ionic reactant, the method corresponds to the traditional method of investigating ion-molecule reactions, IMRs, in a low pressure ion source with a continuous extraction field. This common technique has been reviewed by Franklin [31] and critically evaluated by Henschman [32]. The measurements on IMRs in the $i\text{-C}_4\text{H}_{10}$, N_2O and H_2O systems, were evaluated according to the theoretical treatment of Szabo [33]. The results are given and discussed in Papers I, IV and V, respectively. In this summary a few comments on the results on the IMRs in H_2O will be given.

H_2O^+ is stable in the $\tilde{\text{X}}$, the $\tilde{\text{A}}$ and the lower vibrational levels of the B state [34]. A main conclusion in Paper V is that H_2O^+ initially formed in these states all react with H_2O to give H_3O^+ , and with similar rate constants.

Investigations of IMRs in H_2O , by ionizing with incident Ne^+ (and He^+) gave too high rate constants. It was argued in the paper, that the dominant reaction mechanism is exothermic charge transfer, and that probably no resonant reactions were observed. This interpretation also explained the discrepancy between the breakdown graphs determined with charge transfer [35] and photoelectron-photoion coincidence spectroscopy [34,36].

It has earlier been shown [37] that the formation of H_5O_2^+ by association of a water molecule to H_3O^+ , in a gas at high pressure and in thermal equilibrium is described by a third order rate constant. This implies that two consecutive collisions with neutral molecules should be involved in the reaction, i.e. an initial complex formation followed by a competition between unimolecular decomposition and collisional deactivation. This is according to the mechanism for association reactions [38]. In contrast to this, it was found in Paper V that the intensity of H_5O_2^+ increased with the fifth power of the pressure, while the intensity of H_3O^+ only increased with the square of the pressure. This means that three, instead of two, consecutive collisions are involved in the reaction, unless the residence time of H_3O^+ in the ion source increases linearly with the pressure. This is possible, if the residence time of H_3O^+ is not the free fall time of the ion in an empty source, but is determined by the mobility of the ion. Chong and Franklin [39] encountered such an example while studying clustering reactions in CO. According to them [39,31], free fall calculations are not valid above ca. 100×10^{-3} torr, which is considerably higher than the 3.7×10^{-3} torr used in the low pressure experiments in Paper V.

6. BEAM CHEMICAL IONIZATION

In chemical ionization in a high pressure ion source, the production of reagent ions and the ionization of sample molecules take place in the same gas. The choice of reagent ions is restricted by the ion-molecule chemistry of the carrier gas. For example, in methane mainly CH_5^+ and C_2H_5^+ ionize the sample. In beam chemical ionization, BCI, the reagent ions are prepared in a separate ion source. An almost unlimited number of reagent ions may thus be used. For example, CH^+ , CH_2^+ , CH_3^+ and CH_4^+ ions are easily obtained from methane gas. The sample molecules may be ionized by charge, proton or hydride-ion transfer or by other ion-molecule reactions. The results in paper VI were obtained in a perpendicular type tandem mass spectrometer (Fig. 1) and consequently preferably charge transfer reactions were observed.

Chemical ionization in a tandem mass spectrometer has the following advantages.

Variability of mass spectra

A pure substance may be ionized by several different types of ionization reactions. The extent of fragmentation may be varied by changing the energetics of the reaction. This is illustrated in Paper VI for n-decane and acetophenone. This possibility facilitates identification and structure determination, especially as reagent ions may be changed within milliseconds.

Distinction between isomers

Differences between mass spectra for isomers may be enhanced by using particular incident ions as seen in Papers I-III, and in Paper VI for hexane isomers. Considerable different charge transfer mass spectra of cis- and trans-2-butene were obtained for some incident ions (Paper III), despite that the molecular ions, within experimental uncertainty, have identical fragmentation patterns. The reason for the differences is that the transition probabilities at a specified excitation energy is not the same for the cis and trans isomer. Which incident ions that will give different charge transfer mass spectra for a pair of isomers, may be predicted from the photoelectron spectra.

Selective ionization of mixtures

Selective ionization of components in a mixture can be achieved in certain cases, for example for aromatic compounds in a hydrocarbon mixture. This is shown in the last section in paper VI.

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